



## Reversible and irreversible deactivation of Cu-CHA NH<sub>3</sub>-SCR catalysts by SO<sub>2</sub> and SO<sub>3</sub>



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### ABSTRACT

Sulfur oxides are a common source for the deactivation of Cu-exchanged CHA zeolite based catalysts used for NO<sub>x</sub> reduction in diesel exhausts by selective catalytic reduction with NH<sub>3</sub> (NH<sub>3</sub>-SCR). Since water and possible formation of SO<sub>3</sub> affect the deactivation of Cu-CHA catalysts, the deactivation in the presence of SO<sub>2</sub> or a mixture of SO<sub>2</sub> and SO<sub>3</sub> was studied by measuring the SCR activity in wet and dry gas at 200 and 550 °C. The estimated S-content in the catalysts before and after 4 h regeneration at 550 °C in NO, NH<sub>3</sub>, O<sub>2</sub> and H<sub>2</sub>O was related to the deactivation. The deactivation can be divided into two parts: a reversible deactivation that is restored by the regeneration treatment, and an irreversible part. The irreversible deactivation does not affect the activation energy for NH<sub>3</sub>-SCR and display a 1:1 correlation with the S-content, consistent with deactivation by Cu-sulfate formation. The reversible deactivation results in a lower activation energy and a deactivation that is larger than expected from the S-content. The presence of SO<sub>3</sub> at 200 °C leads to higher reversible and irreversible deactivation, but has no significant impact at 550 °C. Furthermore, the irreversible deactivation is always higher when exposed at 200 °C than at 550 °C, and in wet conditions, compared to a dry feed. The deactivation is predominantly reversible, making regeneration at 550 °C a realistic approach to handle S-poisoning in exhaust systems.

### 1. Introduction

Combustion of diesel fuel in automotive engines produces NO<sub>x</sub> (NO and NO<sub>2</sub>). Due to the environmentally negative impact of NO<sub>x</sub>, emissions of these compounds are subject to strict regulations, which requires NO<sub>x</sub> reduction from the exhaust gas. The current technology for the removal of NO<sub>x</sub> is selective catalytic reduction (SCR) of NO<sub>x</sub> with NH<sub>3</sub>. Apart from an NH<sub>3</sub>-SCR catalyst, a complete diesel exhaust after-treatment system also contains a diesel oxidation catalyst to oxidize CO and unburnt fuel, a particle filter to remove soot, and an ammonia slip catalyst to remove the ammonia not used in the upstream NH<sub>3</sub>-SCR reaction.

The best known NH<sub>3</sub>-SCR catalysts are based on V<sub>2</sub>O<sub>5</sub>, or Cu- or Fe-zeolites. Compared to V<sub>2</sub>O<sub>5</sub>-based catalyst systems, Cu-zeolites generally work well in a broader temperature region (~150–500 °C) [1]. In particular, the better low temperature activity for Cu-zeolites is of interest for cold-start conditions. Combined with the good hydrothermal

stability of small-pore zeolites, these traits have led to commercialization of Cu-zeolites in diesel engine exhaust systems, and Cu-CHA is the current state-of-the-art Cu-zeolite catalyst for diesel emission control.

Another important requirement for NH<sub>3</sub>-SCR catalysts is low susceptibility to SO<sub>2</sub>-poisoning. Diesel fuels contain a small amount of sulfur, and even ultra-low sulfur fuel will result in SO<sub>2</sub> in the exhaust gas. The performance of NH<sub>3</sub>-SCR catalysts, however, can be very sensitive to the presence of SO<sub>2</sub>, even at low concentrations, as in ultra-low sulfur diesel [2]. It is therefore important to know the effect of SO<sub>2</sub> on the performance of an NH<sub>3</sub>-SCR catalysts.

Unfortunately, Cu-zeolite catalysts deactivate more in the presence of SO<sub>2</sub> in the exhaust gas, while Fe-zeolites are less affected by SO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> is not affected [1,3,4]. Consequently, to be able to exploit the potentially better performance of Cu-zeolite catalysts in an exhaust after-treatment system, it is important to understand how the presence of SO<sub>2</sub> influences the performance of these catalysts. Furthermore, it is also important to know to what degree the deactivation of Cu-zeolites

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induced by  $\text{SO}_2$  is reversible versus irreversible.

The current understanding of Cu-zeolite catalyst deactivation by  $\text{SO}_2$ , and Cu-CHA in particular, is that it originates from  $\text{SO}_2$  interaction with the Cu-sites. This can simply be adsorption of  $\text{SO}_2$  or could involve a chemical reaction between the  $\text{SO}_2$  and Cu-sites [2,5–13]. X-ray photoemission and X-ray absorption spectroscopy indicate that the Cu in the ion-exchange positions reacts to form a  $\text{CuSO}_4$ -like species [2]. The formation of sulfates suggests that some oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  takes place. In an after-treatment system, oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  can occur on the diesel oxidation catalyst [2,11], and on the  $\text{NH}_3\text{-SCR}$  catalyst [5]. A higher sulfur uptake and stronger deactivation has been observed in the presence of  $\text{SO}_3$  in the feed gas [2,11]. Therefore, a better understanding of the effect of  $\text{SO}_3$  on the performance of  $\text{NH}_3\text{-SCR}$  catalysts is needed.

Another mechanism for deactivation of  $\text{NH}_3\text{-SCR}$  catalysts is the formation of ammonium sulfate on the catalyst, which restricts access to the active sites. The presence of  $\text{SO}_2$  or  $\text{SO}_3$  in a standard,  $\text{NH}_3$ -containing SCR-gas causes formation of ammonium sulfate, which is a solid below 300 °C, and therefore, deactivation by ammonium sulfate only occurs in the low-temperature range. Ammonium sulfate can be removed by heating the catalyst to above 350 °C, which means that regeneration from this type of deactivation is possible in an exhaust system [5,9,10].

An  $\text{NH}_3\text{-SCR}$  catalyst in a diesel exhaust treatment system is typically operated between 200 and 550 °C, and in the presence of 5–10% water vapor. The effect of temperature on catalyst deactivation by  $\text{SO}_x$  depends on the presence of  $\text{SO}_3$  [2,11]. With  $\text{SO}_2$  only, the deactivation is more severe at 200 °C than at 400 °C, while the opposite trend is observed in the presence of  $\text{SO}_3$  [2,11].

Water also interacts with the Cu ions, changing the environment of and around the active sites in a Cu-CHA catalyst. Water vapor is known to partially hydrolyze the Cu-sites at temperatures below 250 °C [14], affecting the performance for  $\text{NH}_3\text{-SCR}$ . In a similar way, reactions between different Cu-sites with sulfur oxides can be affected by water as well [8,15]. From a mechanistic point of view, the impact of water vapor on the deactivation by  $\text{SO}_2$  and  $\text{SO}_3$  should be understood, with the additional consideration that  $\text{SO}_3$  and  $\text{H}_2\text{O}$  combine and form sulfuric acid below 400 °C [11].

In practice, there are essentially two ways to deal with the presence of  $\text{SO}_x$  in an exhaust gas. The first one is to design the Cu-CHA SCR catalysts in such a way that the amounts of  $\text{SO}_2$  and  $\text{SO}_3$  passing through the system during its lifetime can be accommodated in the system. Alternatively, periodic regeneration strategies must be designed that restore at least a part of the catalytic activity. It is therefore important to know how the presence of  $\text{SO}_2$  and  $\text{SO}_3$  in the exhaust gas stream affects the performance of Cu-CHA catalyst and if regeneration of a Cu-CHA catalyst is possible. In this article, we focus on the effect of the temperature and  $\text{H}_2\text{O}$  and  $\text{SO}_3$  on the  $\text{SO}_x$ -induced deactivation of a monolithic Cu-CHA catalyst for  $\text{NH}_3\text{-SCR}$ . The stability of species formed was studied by comparing the activities of a deactivated catalyst with that after heating to 550 °C, which is a temperature that can be reached in an exhaust system.

## 2. Experimental

### 2.1. Preparation of the catalysts

In this study we used both a Cu-CHA powder catalyst and a monolithic Cu-CHA catalyst. For the powdered catalyst, Cu was introduced into the H-CHA zeolite by ion-exchange for 24 h with an aqueous solution of  $\text{Cu}(\text{CH}_3\text{COO})_2$  (5 mmol/kg) at 20 °C, using 20 g H-CHA zeolite powder in 5 kg solution. After ion-exchange the Cu-CHA was filtered and washed with approx. 20 L MilliQ water, which resulted in a colorless filtrate. The Cu-CHA powder was then dried overnight at 95 °C, and calcined at 550 °C for 3 h. The Si/Al ratio was 14.7 and the Cu/Al ratio was 0.5, corresponding to a Cu-loading of 2.8 wt%, as

determined by ICP-OES.

The monolithic Cu-CHA catalyst was prepared by washcoating a cordierite monolith with a slurry of  $\text{H}_2\text{O}$ , xanthan gum, colloidal silica and Cu-CHA powder. The Cu-CHA powder was prepared by impregnating 1 kg of H-CHA powder (Si/Al = 16.6) with Cu in 1 kg of an aqueous solution of 0.39 mmol/g  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in a rotary evaporator for 4 h at 95 °C. The Cu-loading of the powder was 2.5 wt%, based on the amount of Cu added for the impregnation. After impregnation, the powder was calcined at 550 °C for 3 h. A cordierite monolith ( $D \times L = 25.4 \times 10.2$  cm, 300 cpsi, 0.13 mm wall thickness) was washcoated with the Cu-CHA slurry to a washcoat-loading of 151 g/L. The Cu-CHA/cordierite monolith was dried at 100 °C, and calcined at 550 °C for 3 h.

### 2.2. Catalytic test on powder

The  $\text{NH}_3\text{-SCR}$  activity measurements on the Cu-CHA powder were carried out in a fixed-bed quartz reactor with a 2 mm inner diameter, using 5.0 mg catalyst (150–300  $\mu\text{m}$  sieve fraction) on a dry matter basis. The SCR feed gas composition was 500 ppmv NO, 530 ppmv  $\text{NH}_3$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$  balanced by  $\text{N}_2$ , which we hereafter refer to as “SCR-gas”. The total flow rate used in the measurements was 0.225 NL/min (10 mmol/min, standard conditions:  $T = 0$  °C,  $P = 1$  atm). The outlet gas was analyzed by a Gasmet CX4000 FTIR analyzer.

The Cu-CHA powder exposure to  $\text{SO}_2$  was either done in situ in the reactor at 550 °C for 1 h with 40 ppmv  $\text{SO}_2$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$  balanced by  $\text{N}_2$  with a total flow rate of 0.2 NL/min (9 mmol/min), or ex situ in a tube furnace at 550 °C for 16 h with 100 ppmv  $\text{SO}_2$ , 16%  $\text{O}_2$  balanced by  $\text{N}_2$  with a total flow rate of 0.2 NL/min. Regeneration was always carried out in situ in the reactor at 550 °C with an SCR-gas flow of 0.225 NL/min. 550 °C was chosen, as this is a typical temperature for regeneration of diesel after-treatment systems operating with passive filter regeneration.

### 2.3. Catalytic test on monoliths

With the purpose of studying the impact of temperature and  $\text{H}_2\text{O}$  and  $\text{SO}_3$  gas components on Cu-CHA/cordierite monolith catalyst deactivation by  $\text{SO}_2$ , steady-state  $\text{NO}_x$  conversions were measured before and after  $\text{SO}_x$  exposure, and after regeneration at 550 °C in a laboratory flow reactor system with a horizontal quartz reactor with an inner diameter of 25.4 mm. Upstream and downstream tubing inside surfaces were coated with SilcoNert to minimize adsorption of  $\text{SO}_x$  (and  $\text{NH}_3$ ). Monolith samples of approx.  $20 \times 27$  mm were cut out from the larger prepared sample (sample masses were between 4.5–5.0 g). The reactor temperature was measured at the inlet, inside, and at the outlet of the monolith samples by thermocouples placed in the radial center of the reactor/sample. The steady-state  $\text{NO}_x$  conversions were measured at various temperatures (130–250 °C), at a flow of 8.0 NL/min (357 mmol/min). The SCR feed gas composition was 500 ppmv NO, 530 ppmv  $\text{NH}_3$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$  balanced by  $\text{N}_2$ . The outlet gas was analyzed using a MKS MultiGas 2030 FTIR.  $\text{SO}_x$  exposure was always 3 h in 10%  $\text{O}_2$  with 100 ppmv  $\text{SO}_x$  balanced by  $\text{N}_2$  with a total flow rate of 8.0 NL/min. The variations in the  $\text{SO}_x$  exposure conditions and the assigned sample names, are listed in Table 1. The  $\text{SO}_3$  for the  $\text{SO}_x$  exposures, was produced in an upstream reactor by oxidizing  $\text{SO}_2$  over a Pt/ $\text{Al}_2\text{O}_3$  monolith catalyst. The temperature of the upstream reactor was adjusted to reach a steady-state conversion of  $\text{SO}_2$  of 30%, which was added to the main feed prior to the inlet of the quartz reactor containing the Cu-CHA/cordierite catalyst. Regeneration was carried out in the SCR feed gas at 550 °C, heating at 10 °C/min, for 4 h. In order to check if there were S-species remaining on the samples after regeneration, temperature-programmed desorption (TPD) to 900 °C was carried out after the final  $\text{NO}_x$  conversion measurement that followed the regeneration. The  $\text{SO}_2\text{-TPD}$  was carried out in  $\text{N}_2$  at a flow rate of 8.0 NL/min, and with a temperature ramp at 10 °C/min. The

**Table 1**  
Assigned sample names according to variations in SO<sub>x</sub> exposure conditions.

SO <sub>x</sub> exposure conditions	100 ppm SO <sub>2</sub>	70 ppm SO <sub>2</sub> + 30 ppm SO <sub>3</sub>
5% H <sub>2</sub> O T = 200 °C Dry	SO2-H2O-200	SO3-H2O-200
T = 200 °C 5% H <sub>2</sub> O T = 550 °C Dry	SO2-200	SO3-200
T = 550 °C	SO2-H2O-550	SO3-H2O-550
T = 550 °C	SO2-550	SO3-550

concentrations of H<sub>2</sub>O, NO, NO<sub>2</sub>, NH<sub>3</sub>, SO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> were monitored during regenerations and TPD measurements.

#### 2.4. Evaluation of activity and deactivation

The activities of the catalysts are evaluated by the rate constants, which are derived from the steady-state NO<sub>x</sub> conversion measurements. If we assume that the NH<sub>3</sub>-SCR reaction is first order in NO, the rate constant is given by:

$$k = -\frac{F}{W} \ln(1 - X) \quad (1)$$

where  $F$  is the total molar flow rate,  $W$  is the mass of the Cu-CHA powder in both tested catalysts, and  $X$  is the conversion of NO. The deactivation is expressed as the relative rate constant of a sulfated or regenerated catalyst with respect to the rate constant for the fresh catalyst:

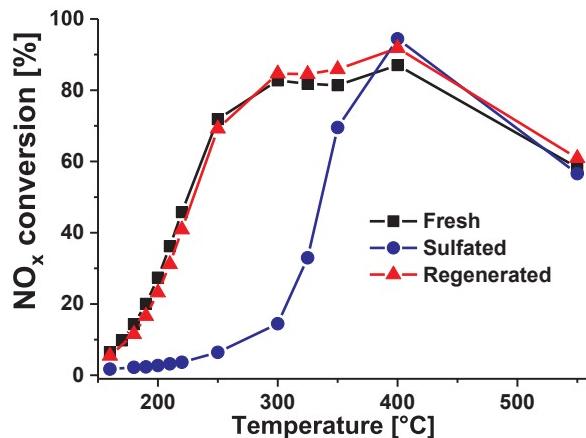
$$\text{Deactivation} = 1 - \frac{k}{k_{\text{fresh}}} = 1 - \frac{A \exp\left(-\frac{E_a}{RT}\right)}{A_{\text{fresh}} \exp\left(-\frac{E_{a,\text{fresh}}}{RT}\right)} \quad (2)$$

Multiplication by 100 then yields the deactivation expressed as a percentage.

### 3. Results

#### 3.1. Powder experiments

The general behavior of a Cu-CHA catalyst upon exposure to SO<sub>2</sub> and regeneration at 550 °C is illustrated in Fig. 1 for the powder catalyst, which shows the measured NO<sub>x</sub> conversions for a fresh catalyst,



**Fig. 1.** NO<sub>x</sub> conversion as function of temperature of a Cu-CHA catalyst (Si/Al = 14.7, Cu/Al = 0.5, and 2.8 wt% Cu) in fresh, sulfated and regenerated state. SCR conditions: 500 ppm NO, 530 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, 5% H<sub>2</sub>O, N<sub>2</sub> balance to 0.225 NL/min on 5.0 mg catalyst in reactor with an inner diameter of 2 mm. SO<sub>x</sub> exposure conditions: 100 ppm SO<sub>2</sub>, 16% O<sub>2</sub>, N<sub>2</sub> balance to 0.2 NL/min for 16 h at 550 °C. Regeneration conditions: 4.6 h at 550 °C in SCR-gas.

after exposure to 100 ppm SO<sub>2</sub> at 550 °C (sulfated), and after regeneration at 550 °C in SCR-gas (regenerated).

The most significant effect of exposure to SO<sub>2</sub> is seen in the lower temperature range, up to 300 °C, where NO<sub>x</sub> conversion was significantly inhibited compared to the fresh sample. Above 300 °C, the NO<sub>x</sub> conversion increases rapidly with temperature to slightly above the conversion measured for the fresh catalyst. After regeneration by heating to 550 °C, the conversion above 300 °C was slightly higher, but close to that of the fresh catalyst. Below 300 °C, the conversion remained slightly below that of the fresh catalyst. This shows that exposure to SO<sub>2</sub> results mainly in deactivation of the low-temperature ( $T < 350$  °C) activity of the catalyst, which is consistent with previously reported observations [5,9,11], and regeneration at 550 °C does not fully restore the activity below 300 °C entirely.

To investigate if the incomplete regeneration at 550 °C is due to a too short regeneration time, the regeneration process was monitored by heating the samples at 550 °C for a total of 12 h in intervals, where after each interval the activity at 200 °C was re-evaluated. Fig. 2A shows the measured activity at 200 °C obtained in this way, which indicates that a stable activity level is reached at about 75–80% of the original activity after approximately 4 h of regeneration. This means that a complete regeneration by heating at 550 °C seems not possible.

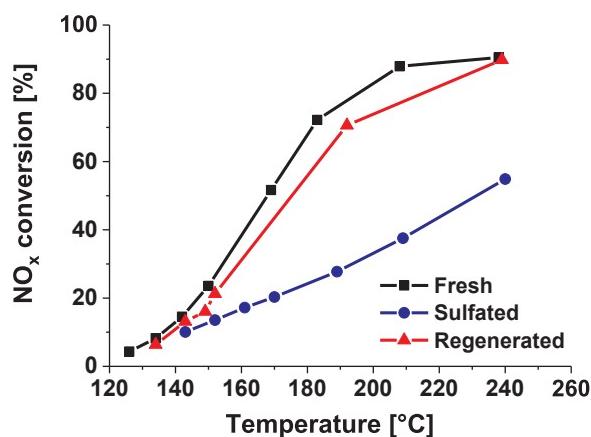
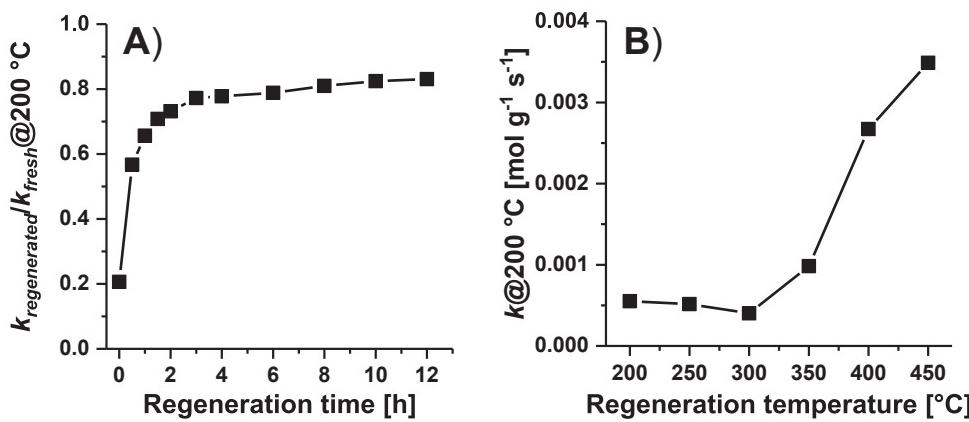
Fig. 1 shows that the NO<sub>x</sub> conversion over a catalyst after exposure to SO<sub>2</sub> increases slightly with temperature up to 300 °C, followed by a steep increase. To determine whether the slight increase below 300 °C is due to a normal temperature dependency of a possible residual activity, or to a slow regeneration in this temperature range, we checked the influence of the temperature on activity of a Cu-CHA catalyst at 200 °C. To do this measurement, a single catalyst sample deactivated by SO<sub>2</sub> was sequentially exposed to heating for 2 h in 5% H<sub>2</sub>O/10% O<sub>2</sub>/N<sub>2</sub> at a chosen temperature between 200 and 450 °C in increasing order, and then cooled down to 200 °C where the NO<sub>x</sub> conversion was then re-measured. Fig. 2B shows the rate constant at 200 °C, determined according to Eq. (1) as a function of the heating temperature. The rate constant at 200 °C does not increase by heating to a temperature of 300 °C or lower, which clearly indicates that the regeneration of a catalyst exposed to SO<sub>2</sub> does not start below 300 °C, and the slight increase in conversion in Fig. 1 is therefore due to the temperature dependence of a residual activity. This also means that measured SCR activities after exposure to SO<sub>2</sub> are not affected by regeneration if the measurements are done at 300 °C or lower.

The observation that the activity after SO<sub>2</sub> exposure cannot be completely restored by heating to 550 °C indicates that there are different forms of deactivation. Based on these data, we define these different forms of deactivation as follows: the part of the deactivation that can be restored by 4 h heating at 550 °C will be referred to as the *reversible deactivation*, and the remaining part as the *irreversible deactivation*. The *total deactivation* is the sum of these two contributions. An activity measured after exposure to SO<sub>x</sub> before regeneration, represents the total deactivation, the irreversible deactivation is found from the activity after regeneration. The reversible deactivation can then be determined as the difference in activity of a SO<sub>x</sub>-treated catalyst before and after regeneration. The following expression is used to determine the relative reversible deactivation with respect to the activity of the fresh catalyst:

$$1 - \frac{k_{\text{sulfated}}}{k_{\text{fresh}}} = \text{Reversible deactivation} + \left(1 - \frac{k_{\text{irreversible}}}{k_{\text{fresh}}}\right) \quad (3)$$

#### 3.2. Monolith experiments

The effects of SO<sub>3</sub>, water and SO<sub>x</sub> exposure temperature on the catalyst deactivation and regeneration was studied by measurement of NO conversions over Cu-CHA/cordierite monolith samples after exposure to SO<sub>x</sub> at the conditions listed in Table 1, and after subsequent

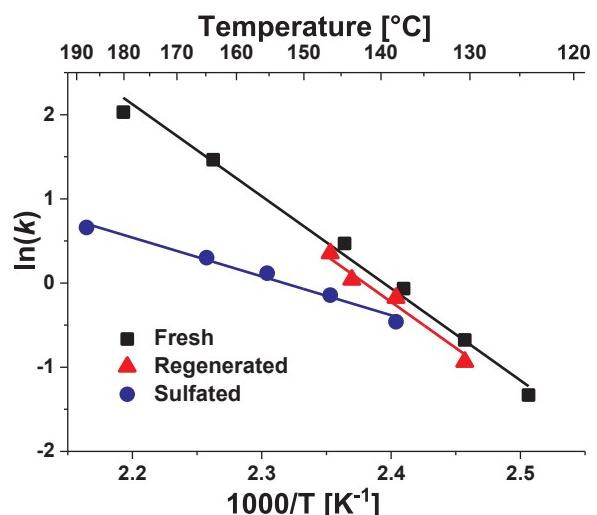


**Fig. 3.**  $\text{NO}_x$  conversion as function of temperature of a Cu-CHA/cordierite catalyst (Cu-CHA: Si/Al = 16.6, 2.5 wt% Cu) in fresh, sulfated and regenerated state. SCR conditions: 500 ppmv NO, 530 ppmv  $\text{NH}_3$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ ,  $\text{N}_2$  balance to 8.0 NL/min on  $20 \times 27$  mm cylindrical monolith catalyst in reactor with an inner diameter of 25.4 mm.  $\text{SO}_x$  exposure conditions: 100 ppmv  $\text{SO}_2$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ ,  $\text{N}_2$  balance to 8.0 NL/min for 3 h at  $200^\circ\text{C}$ . Regeneration conditions: 4 h at  $550^\circ\text{C}$  in SCR-gas.

heating at  $550^\circ\text{C}$ . In all these measurements, the deactivation and regeneration followed the same general trend as observed for the Cu-CHA powder. Fig. 3 shows the measured  $\text{NO}_x$  conversion in the range  $150\text{--}250^\circ\text{C}$  after deactivation in wet  $\text{SO}_2$  without  $\text{SO}_3$  as an example. Exposure to  $\text{SO}_2$  leads to a lower  $\text{NO}_x$  conversion, which is mostly restored by heating at  $550^\circ\text{C}$ . It is noted that all activity measurements shown in Fig. 3 are obtained below  $300^\circ\text{C}$ , and are therefore not influenced by regeneration during the measurements.

Due to variations in temperature in the different measurements, a common base for comparison of the measured  $\text{NO}_x$  conversions is needed. To this end, Arrhenius plots were constructed; Fig. 4 shows the Arrhenius plot based on the data in Fig. 3, and represents the general observation for all samples (see supporting information). For all conditions, the slopes of the fresh and regenerated states of the catalyst are nearly the same, while the slope of the sulfated state of the catalyst is always smaller. Our interpretation is that the activation energies for the fresh and regenerated catalysts are the same, and the activation energy was determined from the combined data points of the fresh and regenerated states. Consequently, the differences in activity for fresh and regenerated catalysts are translated to differences in the pre-exponential factor. The relative irreversible deactivation then becomes independent of the temperature for the conditions used here. The assignment of irreversible deactivation to changes in the pre-exponential factor implies a mechanism in which deactivation is caused by loss of active sites, without major changes in the chemistry of the reaction.

The situation is different for the sulfated catalysts, which consistently have lower activation energy than the fresh and regenerated



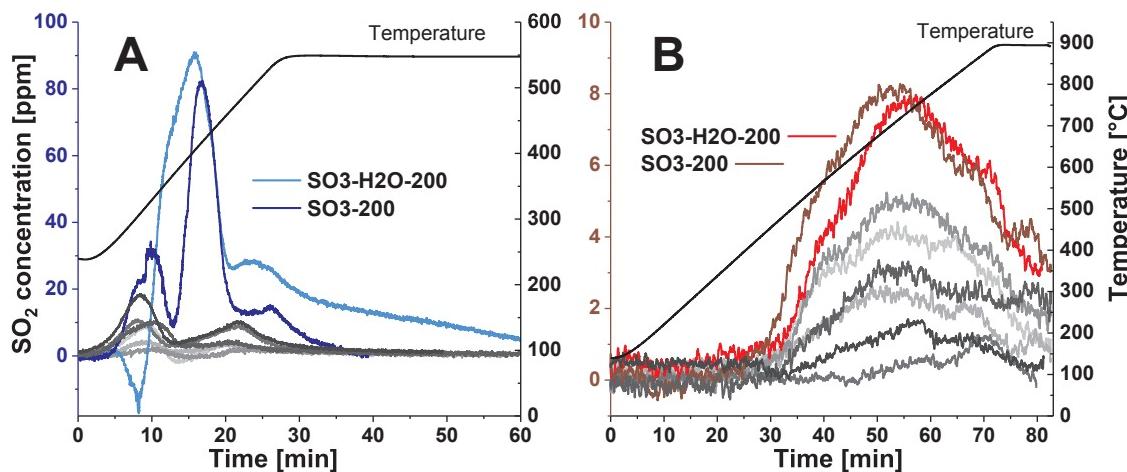
**Fig. 4.** Arrhenius plot of a Cu-CHA/cordierite catalyst (Cu-CHA: Si/Al = 16.6, 2.5 wt% Cu) in fresh, sulfated and regenerated state.  $\text{SO}_x$  exposure conditions: 100 ppmv  $\text{SO}_2$ , 10%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ ,  $\text{N}_2$  balance to 8.0 NL/min for 3 h at  $200^\circ\text{C}$ . Regeneration conditions: 4 h at  $550^\circ\text{C}$  in SCR-gas.

**Table 2**

Activation energies of fresh ( $E_{a,\text{fresh}}$ ) and sulfated ( $E_{a,\text{sulfated}}$ ) states of the tested Cu-CHA/cordierite catalysts, and the ratios of  $E_{a,\text{sulfated}}/E_{a,\text{fresh}}$ .

Sample	$E_{a,\text{fresh}}$ [kJ mol <sup>-1</sup> ]	$E_{a,\text{sulfated}}$ [kJ mol <sup>-1</sup> ]	$E_{a,\text{sulfated}}/E_{a,\text{fresh}}$ (min-max)
SO2-H2O-200	91 ± 8	38 ± 5	0.33–0.53
SO2-200	99 ± 3	53 ± 2	0.50–0.58
SO2-H2O-550	90 ± 7	53 ± 1	0.54–0.65
SO2-550	59 ± 3	30 ± 5	0.41–0.63
SO3-H2O-200	80 ± 26	15 ± 2	0.12–0.32
SO3-200	115 ± 16	39 ± 4	0.27–0.45
SO3-H2O-550	97 ± 4	39 ± 1	0.38–0.43
SO3-550	76 ± 5	31 ± 1	0.36–0.45

catalysts. Table 2 lists the activation energies for the fresh and sulfated samples, and the ratio of the two values. The lower activation energies of the sulfated catalysts also mean that the measured reversible deactivation depends on the temperature of the SCR activity measurement. A change in activation energy cannot be due to a loss of active sites only. Phenomena that could change the activation energy are a change in the chemistry of the  $\text{NH}_3\text{-SCR}$  reaction and diffusion limitations of the  $\text{NH}_3\text{-SCR}$  reaction rate in the zeolite crystals after exposure to  $\text{SO}_x$ . In the limit of strong pore diffusion limitations, the observed activation energy will be half the value of the intrinsic value. In principle, this is an option for the samples treated with  $\text{SO}_2$  alone. For the samples



**Fig. 5.**  $\text{SO}_2$  desorption spectra for sulfated Cu-CHA/cordierite catalysts, A) during heating to 550 °C at 10 °C/min in SCR-gas with a total flowrate of 8.0 NL/min, after sulfation, B) during heating to 900 °C at 10 °C/min in 8.0 NL/min  $\text{N}_2$ , after sulfation and regeneration for 4 h at 550 °C. Curve-smoothing has been applied on the curves in B, using an adjacent-averaging method. In both A and B, legends are only provided for the catalysts exposed to  $\text{SO}_3$  at 200 °C. Plots containing legends for all catalysts can be found in supporting information.

treated with  $\text{SO}_3$ , the activation energy ratios are lower than 0.5, which cannot be explained by internal diffusion limitations alone, suggesting that chemical effects are more pronounced in this case.

### 3.3. Desorption of $\text{SO}_2$

To determine the amount of sulfur deposited on the catalysts,  $\text{SO}_2$  concentrations were measured during the regeneration up to and at 550 °C in SCR-gas, and during heating to 900 °C in  $\text{N}_2$  after all activity measurements. The measured  $\text{SO}_2$  desorption during the regeneration to 550 °C, shown in Fig. 5A, is related to the reversible deactivation. No  $\text{SO}_3$  or  $\text{H}_2\text{SO}_4$  desorption was observed during the regeneration. Clearly, the two samples exposed to  $\text{SO}_3$  at 200 °C stand out with a substantially higher  $\text{SO}_2$  desorption around 400 °C. Since the two catalysts exposed to  $\text{SO}_2$  at 200 °C did not show a similar high  $\text{SO}_2$  desorption around 400 °C, the higher desorption of  $\text{SO}_2$  from the two catalysts exposed to  $\text{SO}_3$  at 200 °C must be due to decomposition of  $\text{SO}_3$  or sulfates [2,11,12]. The desorption temperature of 400 °C is about 200–250 °C lower than the decomposition temperature of bulk Cu sulfate [12]. This indicates that only little Cu sulfate is formed from  $\text{SO}_3$  at 200 °C, or that the Cu-sulfate species formed this way in the Cu-CHA catalysts are less stable than bulk Cu-sulfate.

All other samples, exposed to  $\text{SO}_2$  at 200 °C or  $\text{SO}_2 + \text{SO}_3$  at 550 °C, show similar  $\text{SO}_2$  desorption peaks at approx. 300 °C and 475 °C. This means that exposure to  $\text{SO}_3$  at 550 °C essentially results in similar sulfur species as exposure to  $\text{SO}_2$  at 200 or 550 °C, and the influence of water is limited. The observed desorption temperatures are consistent with decomposition of ammonium sulfate [5] and sulfuric acid [12,15]. Ammonium sulfates can possibly have been formed by the exposure of the sulfated samples to  $\text{NH}_3$  during the SCR activity measurement directly after the  $\text{SO}_x$  exposure [10], which would imply a reaction of the adsorbed sulfur species and ammonia.

Fig. 5B shows the desorption of  $\text{SO}_2$  during heating in  $\text{N}_2$  to 900 °C after  $\text{SO}_x$  exposure and regeneration, which represents the sulfur species associated with irreversible deactivation. The catalysts exposed to  $\text{SO}_3$  at 200 °C show again the largest amount of  $\text{SO}_2$ . The desorption peak is centered around 675 °C for all samples, indicating that the same species is formed in all catalysts, but in different amounts, dependent on the conditions for  $\text{SO}_2$  exposure. The temperature of 675 °C is consistent with the irreversible deactivation being related to formation of Cu-sulfate [12].

From integration of the curves in Fig. 5, the amounts of sulfur in the sulfated and regenerated catalysts can be estimated, and we highlight the differences in sulfur content between the samples exposed to  $\text{SO}_3$  at 200 °C and the other samples. The quality of the measured  $\text{SO}_2$

concentrations during regeneration is poor, but the differences between the samples exposed to  $\text{SO}_3$  at 200 °C and the other ones are quite clear. We also note that no  $\text{SO}_3$  was detected during the temperature programmed desorption, and no sulfur was found in an ICP-OES analysis of the catalysts after heating to 900 °C. This means that the amounts of sulfur detected in the desorption measurements accounts for all sulfur present in the catalysts.

Table 3 lists the  $\text{SO}_2/\text{Cu}$  ratios related to the reversible and irreversible deactivation as derived from integration of the  $\text{SO}_2$  desorption curves and the Cu content in the zeolite. The  $\text{SO}_2/\text{Cu}$  ratios of all samples are below 1, which indicates that not all Cu has reacted with  $\text{SO}_x$ , which would be required for complete formation of Cu-sulfate. The  $\text{SO}_2/\text{Cu}$  ratio after exposure to  $\text{SO}_3$  at 200 °C in dry gas is 0.58, and 0.90 in the presence of water, and 70–80% of this amount is released during regeneration at 550 °C. In all other cases, the  $\text{SO}_2/\text{Cu}$  ratio is 0.1–0.2.

### 3.4. Influence of $\text{SO}_2/\text{SO}_3$ , water and temperature on deactivation

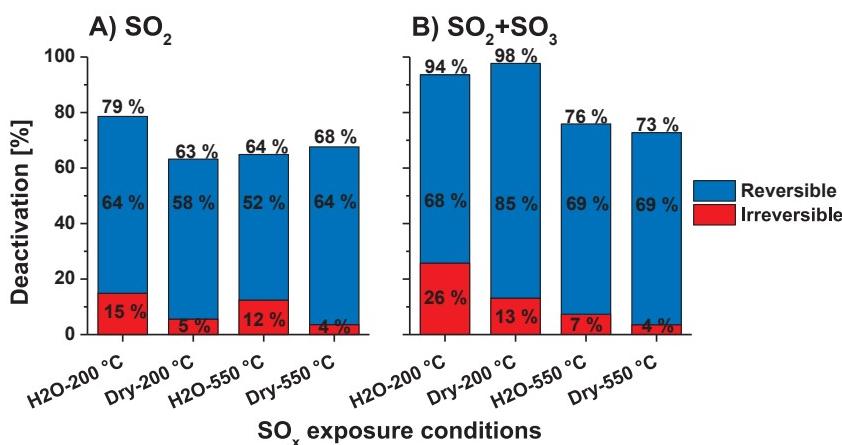
Having established the general trends in performance and sulfur content after sulfation, and regeneration of the Cu-CHA catalyst, we now turn our attention to the effects of temperature of  $\text{SO}_x$  exposure, and the presence of water or  $\text{SO}_3$ . Fig. 6A and B show the reversible and irreversible deactivation for the samples exposed to  $\text{SO}_2$  only and  $\text{SO}_2 + \text{SO}_3$ . The reversible deactivation was derived from interpolation of the activity data to 180 °C, using the Arrhenius plots given in Fig. 2 and supporting information. The deactivation is given as a percentage according to Eq. (2).

The effect of  $\text{SO}_3$  on deactivation is most noticeable with  $\text{SO}_x$  exposure at 200 °C, leading to significantly stronger deactivation, compared to exposure to  $\text{SO}_2$  alone both in dry and wet feed gases. At 550 °C, there is no apparent influence of  $\text{SO}_3$  in the feed gas. This

**Table 3**

The reversible, irreversible and total  $\text{SO}_2/\text{Cu}$  ratios of all Cu-CHA/cordierite catalyst samples.

Sample	Reversible $\text{SO}_2/\text{Cu}$	Irreversible $\text{SO}_2/\text{Cu}$	Total $\text{SO}_2/\text{Cu}$
SO <sub>2</sub> -H <sub>2</sub> O-200	0.07	0.09	0.16
SO <sub>2</sub> -200	0.04	0.05	0.09
SO <sub>2</sub> -H <sub>2</sub> O-550	0.04	0.12	0.16
SO <sub>2</sub> -550	0.10	0.02	0.12
SO <sub>3</sub> -H <sub>2</sub> O-200	0.74	0.16	0.90
SO <sub>3</sub> -200	0.40	0.18	0.58
SO <sub>3</sub> -H <sub>2</sub> O-550	0.09	0.08	0.17
SO <sub>3</sub> -550	0.13	0.03	0.16



shows that the specific deactivation by  $\text{SO}_3$  is most important in the lower temperature range, and that the effect of  $\text{SO}_3$  on deactivation is related to the pronounced decomposition of  $\text{SO}_3$  or sulfate at  $400^\circ\text{C}$ , as shown in Fig. 5A.

The presence of  $\text{H}_2\text{O}$  during  $\text{SO}_x$  exposure always leads to higher irreversible deactivation than the corresponding dry  $\text{SO}_x$  exposure condition, but appears to have no consistent influence on reversible deactivation. With respect to the impact of temperature, irreversible deactivation is always greater in the samples exposed at  $200^\circ\text{C}$  than the corresponding sample exposed at  $550^\circ\text{C}$ , whereas no consistent impact of temperature is observed on reversible deactivation. The general picture that emerges is that the presence of  $\text{SO}_3$  and water at  $200^\circ\text{C}$  has a stronger effect on the deactivation than at  $550^\circ\text{C}$ , in particular on irreversible deactivation.

#### 4. Discussion

The similar activation energies in the SCR reaction for the fresh and regenerated states of the catalysts indicates that irreversible deactivation is the result of having fewer active sites available, and the desorption temperature for  $\text{SO}_2$  from the regenerated catalysts points to the formation of Cu-sulfate. If Cu-sulfate formation is the cause of deactivation, a 1:1 correlation should exist between the irreversible deactivation and the sulfur content. Fig. 7 shows the measured irreversible deactivation as a function of the  $\text{SO}_2/\text{Cu}$  ratio, derived from the corresponding  $\text{SO}_2$  desorption measurements in Fig. 5B, together with the line for the 1:1 correlation. The measured irreversible deactivation actually follows the 1:1 correlation with the sulfur content fairly well,

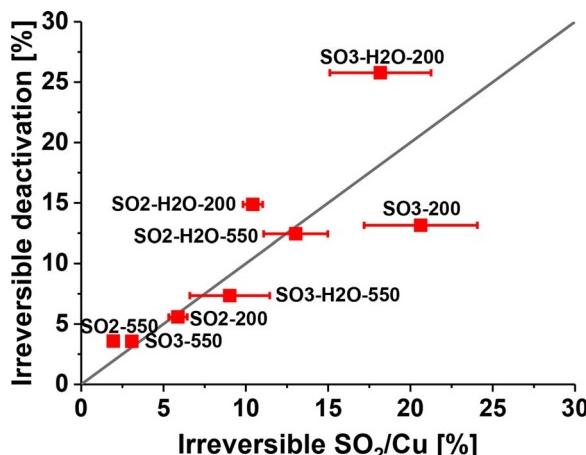


Fig. 7. The irreversible deactivation for the Cu-CHA/cordierite catalysts, determined after  $\text{SO}_x$  exposure and regeneration for 4 h at  $550^\circ\text{C}$ , plotted as function of the  $\text{SO}_2/\text{Cu}$  ratio of the irreversible S-species.

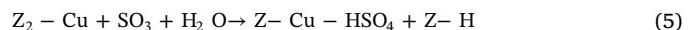
Fig. 6. The reversible deactivation (blue bars), irreversible deactivation (red bars) and total deactivation (sum of red and blue bars) plotted for each  $\text{SO}_x$  exposure condition of the Cu-CHA/cordierite catalysts. A) samples exposed to 100 ppmv  $\text{SO}_2$ , B) samples exposed to 70 ppmv  $\text{SO}_2$  and 30 ppmv  $\text{SO}_3$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

corroborating the idea that Cu-sulfate formation is responsible for the irreversible deactivation [2,5–13].

A way to envision the irreversible deactivation by formation of a Cu-sulfate species is a reaction of  $\text{SO}_3$  with a Cu-ion balanced by a single Al and a hydroxide ligand (Z-Cu-OH), as in reaction Scheme (4).



In this case, the hydroxide ligand provides the oxygen required for formation of sulfate. A  $\text{Cu}^{2+}$  ion balanced by two Al-sites ( $\text{Z}_2\text{-Cu}$ ) does not have the hydroxide ligand, but this does not necessarily mean that these Cu-species are incapable of sulfate formation. In the presence of water, a  $\text{Z}_2\text{-Cu}$  can react to a Z-Cu-OH and a Brønsted acid site [14], and the Z-Cu-OH can then react further with  $\text{SO}_3$  according to reaction Scheme (4). The overall reaction then becomes:



A similar scenario is a reaction with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and a  $\text{Z}_2\text{-Cu}$  site, where the sulfuric acid is formed by reaction of  $\text{SO}_3$  and water. Either way, the presence of water would facilitate formation of Cu-sulfate as this leads to a higher amount of Z-Cu-OH-sites compared to dry conditions. The suggested reaction schemes then offer an explanation for the increase in irreversible deactivation in the presence of water. This means that a model that describes the irreversible deactivation by formation of Cu-sulfate is also consistent with the observed effects of the presence of water.

A comparison of measured deactivation and the sulfur content for the sulfated catalysts reveals a different behavior for reversible deactivation. Fig. 8 shows the total deactivation of the sulfated catalysts as a function of their total  $\text{SO}_2/\text{Cu}$  ratios. Clearly, there is no consistent 1:1

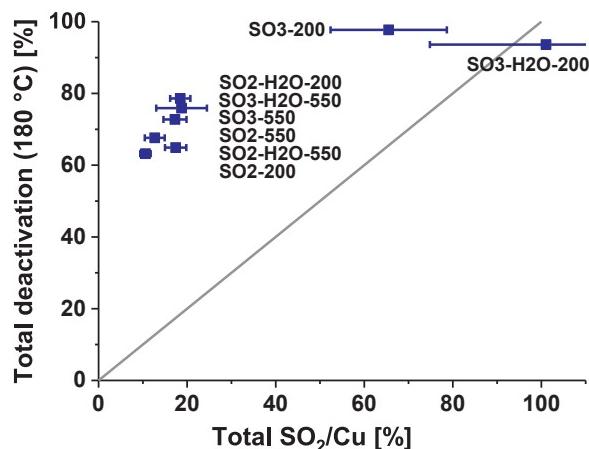
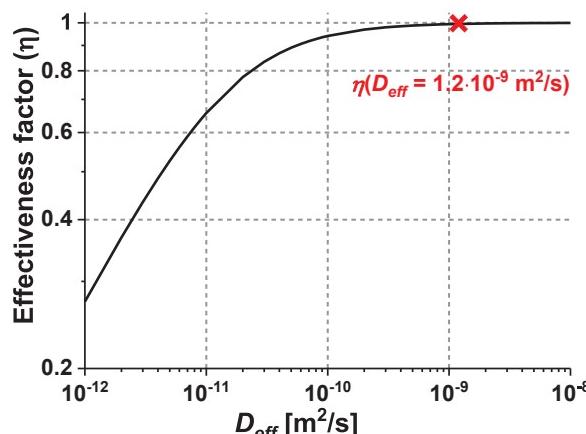


Fig. 8. The total deactivation for the Cu-CHA/cordierite catalysts, determined after  $\text{SO}_x$  exposure, plotted as function of the  $\text{SO}_2/\text{Cu}$  ratio of the total S-species.



**Fig. 9.** Double logarithmic plot of the internal effectiveness factor in the zeolite crystals,  $\eta$ , at 180 °C, as a function of the effective diffusion coefficient,  $D_{\text{eff}}$ .  $\eta$  based on experimental values for  $D_{\text{eff}}$  of NH<sub>3</sub> in a Cu-CHA catalyst in the range 0–100 °C, is marked, which indicates that the reaction in the fresh catalyst is not limited by diffusion of reactants.

dependence of the total deactivation on SO<sub>2</sub>/Cu ratio, with only small SO<sub>2</sub>/Cu ratios, between 10 and 20%, leading to degrees of deactivation as high as 60–80%. This indicates that the loss of activity in this case is not caused by a direct interaction of a single sulfur atom with a single Cu ion, as the measured deactivation is 5–10 times higher than expected from a 1:1 correlation.

The lower activation energies of the sulfated catalysts might be due to formation of internal diffusion limitations induced by SO<sub>x</sub> deactivation, which can play a role in the deactivation process. In case of increased diffusion limitations, the effectiveness factor should become lower in addition to the loss of sites, resulting in an overall deactivation that is higher than the fraction of Cu sites in contact with sulfur. This agrees, at least qualitatively, with the results shown in Fig. 8. To evaluate a possible effect of diffusion limitations, the effectiveness factor,  $\eta$ , was calculated for the fresh catalyst, assuming spherical zeolite crystals and first order reaction kinetics in NO. For the calculations, the crystal radius was set to 0.5 μm, which is a reasonable value given that the crystal size of the zeolite is on the order of 1 μm. A further description of the calculation of the effectiveness factor is given in supporting information. Fig. 9 shows the effectiveness factor as a function of the effective diffusion coefficient,  $D_{\text{eff}}$ , at 180 °C. By extrapolation of experimentally determined values for effective diffusion coefficients for NH<sub>3</sub> in a Cu-CHA catalyst, using the corresponding activation energy [16], we find a diffusion coefficient of 1.2 · 10<sup>-9</sup> m<sup>2</sup>/s. Using this diffusion coefficient, Fig. 9 shows that the effectiveness factor for the fresh catalyst is close to 1. This implies that no internal diffusion limitation is expected in the crystals of the fresh catalyst. Because the activation energy of the regenerated catalysts is the same as for the fresh, diffusion effects can be excluded for the irreversible deactivation as well.

If the reduction of the effective activation energy to half the intrinsic value would be due to diffusion limitations, the effectiveness factor should decrease to be lower than 0.8, where there is a linear relationship between  $\log(\eta)$  and  $\log(D_{\text{eff}})$  resulting in a straight line in Fig. 9. According to Fig. 9, to obtain an effectiveness factor of 0.8, a decrease of the diffusion coefficient by about a factor of 100 would be required. This would mean that the small amount of sulfur, corresponding to less than 20% coverage of the Cu-sites, reduces the diffusion coefficient by a factor of 100. This seems unlikely, also taking into account that a similar sulfur content in the regenerated catalysts does not affect the activation energy and diffusion.

Alternatively, pore-blocking by possible formation of ammonium sulfates may be considered as a cause for the reversible deactivation behavior. We note that the sulfated catalysts are exposed to SO<sub>2</sub>

without ammonia present, and therefore, the resulting sulfur species is most likely bound to the Cu-ions [13]. If ammonium sulfate is formed by subsequent exposure to ammonia, this implies that the ammonium sulfate species is also located close to the Cu-ions. The SO<sub>2</sub>/Cu ratios in the sulfated catalysts is about 0.15 (except in those exposed to SO<sub>3</sub> at 200 °C), which is similar to the SO<sub>2</sub>/Cu ratio in some of the regenerated catalysts, where it was argued that there is no diffusion limitation. Therefore, it seems unlikely that the presence of these fairly small amounts of ammonium sulfate effectively block access to most of the zeolite. At present, the question of how the limited amount of sulfur can have such a strong impact on the reversible deactivation remains unanswered.

Having ruled out diffusion as a cause for reversible deactivation, the lower activation energy must then be related to changes in the chemistry. An interesting concept is Cu being able to form a mobile diamine species at SCR conditions. These mobile Cu-diamine species are important for the low-temperature activity of Cu-CHA catalysts [17–20]. Possibly, the reversible deactivation by sulfur oxide species inhibits the formation of these mobile Cu diamine complexes, thereby lowering the mobility of Cu and the NH<sub>3</sub>-SCR activity, which might lead to the observed high degree of reversible deactivation with low amounts of sulfur.

Finally, our data clearly show that exposure to SO<sub>x</sub> at lower temperatures result in the largest deactivation. However, most of the catalytic activity can be regained by heating to 550 °C, even after exposure to SO<sub>3</sub> at 200 °C. This is an interesting result from an application point of view, since it indicates that regeneration strategies based on heating to easily obtainable temperatures in exhaust systems are a feasible solution to handle deactivation of Cu-zeolites by SO<sub>2</sub> and SO<sub>3</sub> [10,13].

## 5. Conclusion

To evaluate different aspects of sulfur poisoning of NH<sub>3</sub>-SCR activity, Cu-CHA catalysts were exposed to SO<sub>2</sub> or a 70:30 mixture of SO<sub>2</sub> and SO<sub>3</sub>, in dry or moist conditions and at low and high temperature, and were evaluated before and after regeneration at 550 °C. After SO<sub>x</sub> exposure, a high degree of deactivation is observed at temperatures below 300 °C. A major part of this deactivation is reversible by heating to 550 °C for 4 h, while a smaller, but appreciable, level of irreversible deactivation remains.

The mechanisms behind the reversible and irreversible deactivation differs. Irreversible deactivation is proportional to the sulfur content in the catalyst and consistent with the formation of a Cu-sulfate species. Reversible deactivation is not proportional to the sulfur content, and shows a strong deactivation already at low SO<sub>2</sub>/Cu ratios.

The presence of water always increases irreversible deactivation, but has no apparent effect on reversible deactivation. Exposure to SO<sub>x</sub> at 200 °C, always leads to a higher level of irreversible deactivation compared to exposure at 550 °C. The presence of SO<sub>3</sub> at 200 °C leads to significantly stronger deactivation; at 550 °C, deactivation by SO<sub>3</sub> is not significantly different from that by SO<sub>2</sub>. Regeneration of Cu-CHA exposed to SO<sub>3</sub> at 200 °C is accompanied by a decomposition of SO<sub>3</sub> and release of SO<sub>2</sub> around 400 °C.

In all experiments, the reversible deactivation accounts for most of the total deactivation, which makes regeneration by heating to 550 °C, an easily obtainable temperature in exhaust systems, a realistic approach to deal with deactivation by SO<sub>x</sub>.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apcatb.2017.12.018>.

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